Mineral Identification by X-ray Diffraction

1. Introduction

X-ray powder diffraction (XRD) is a widely used technique to identify crystalline materials, both inorganic and organic. Because it is a non-destructive method it commonly is used to scan large numbers of samples for mineral components and then select those samples that require additional characterization. The method can also determine many properties of materials in detail, including identification of mineral phases, determine unit cell dimensions, measure stress and strain in crystals, and determine mineral purity. More advanced procedures allow this method to determine crystal structures, quantify mineral and amorphous components of rocks, as well as numerous other measurements on specialized sample types such as thin films, pharmaceuticals, and polycrystalline materials. In order to conduct any of these studies, the mineral phases in the sample must be identified. This method applies to identification of phases in randomly oriented powder XRD scans and oriented mounts of various particle size fractions.

A crystalline material is a solid whose constituent atoms are arranged in an ordered pattern extending in all three spatial dimensions and thus have sets of repeating planes through the structure. An X-ray beam is incident on a sample of material to be analyzed. The beam is scattered from the many crystallographic planes in the solid. When the angle of beam incidence and wavelength result in coherent diffraction from crystal lattice planes, a detector on the opposite side of the sample from the beam source records an increased intensity of the scattered radiation. The plot of the intensity relative to the angle produces a series of intensity peaks that provide the input for interpretation. This pattern of peaks – diffractogram- is the basis of XRD analysis.

There are two basic methods of identifying mineral phases in an XRD scan. The first and most commonly used method is to compare the diffraction peaks in the unknown material scan to patterns of known standards of pure mineral phases or calculated XRD patterns of minerals. There are numerous published databases of powder diffraction data which may be augmented by in-house standards. Phase identification of a scan typically follows the sequence of matching the most intense peaks in the unknown scan to reference minerals and then searching the remaining portion of the pattern for minor and trace phase matches. The second identification method involves collecting high quality chemical analyses of the material and then using published calculations, either by hand or employing software, to determine the crystal structure of the phases and assign elements, lattice site occupancy, and coordination within a crystal lattice. This second method is used primarily for single crystal, high purity, and (or) powder mixtures having only two or three mineral components.

Currently the Central Energy Resources Science Center uses three software programs for whole-rock mineral identification, including MDI Jade[1], PANalytical Highscore Plus, and MDI ClaySim. Each software package has strengths and weaknesses relative to searching mineral databases or simulating X-ray patterns.

Finally, it must be pointed out that a user unfamiliar with X-ray diffraction can complete only the simplest steps of mineral identification by XRD. A pure phase, and possibly some minor phases in a sample, may be identified following this procedure. As the mineral content decreases, the need for the user to have higher levels of experience increases to successfully identify minor and trace components. This level of interpretation is considered an "art" and requires experience with both the instrumentation to identify artifacts of the instrument configuration and scan parameters, and resolve issues due to interference.

Powder diffraction databases contain several hundred thousand reference cards, many of them collected for specific phases with substitutions or non-standard temperature and pressure conditions. The analyst must be able to decipher which reference minerals are appropriate for a specific sample. Often, other data sets and information are considered with the XRD data to constrain the list of possible phases.

XRD is not a self-taught method. Here in the USA there are two organizations devoted to providing researchers with hands-on training, namely the International Center for Diffraction Data (ICDD) and the National Institute of Standards and Technology (NIST) which maintains the Inorganic Crystal Structure Database (ICSD).

2. **Interfaces with Other Methods**
   This method interfaces with EGL Work Instruction 05, 06, and (or) 07 for scanning samples on the Panalytical X'pert Pro, Scintag X1, Siemens D500 X-ray diffractometers respectively, and with EGL Work Instruction 01 and 02 for loading samples into holders.

3. **Materials and Equipment**
   a. Software
      i. Software must be capable of loading diffractometer output files, index the diffraction peaks, fit and strip (subtract) the background and K-α2 radiation from the diffraction pattern, and search a database of reference minerals of measured or simulated whole patterns.
      ii. Powder diffraction database

[1] Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

4. Procedure

The basic steps to complete a mineral identification are given below. Both MDI Jade and Highscore Plus software have routines that automate portions of any or all the steps.

1. Launch the software package for the analysis.
2. From within the software package, open the XRD scan of interest.
3. Run the "fit background" routine in the software adjusting parameters (sampling points, fit type, background offset); if necessary modify the background manually to improve the fit, take into account amorphous humps, or remove instrument artifacts.
4. Remove (subtract) the background from the original scan that includes the ability to remove diffraction intensity attributed to K-alpha 2 radiation.
5. Run a peak search routine to identify the two-theta position (or d-spacing) and intensity of all peaks in the scan. This step is not necessary for software based searches but can be helpful for manual searches.
6. Set up and run a search routine:
    i. Select the database of standard patterns or "subfile" to be searched
    ii. Set criteria that may limit the search, including chemistry restrictions (composition, stoichiometry, crystallographic parameters, etc)
    iii. Set threshold criteria as needed, such as two-theta error window, intensity matching, minimum number of matching peaks present.
    iv. Run the search routine
7. The output of the search routine will yield a list of minerals, sorted by a "Figure of Merit" score based on the selected search criteria.
    i. Starting with the first mineral on the list, compare the peaks in the reference pattern (both position and intensity) to the peaks in the unknown.
    ii. To determine if a mineral is present in the unknown, consider the following factors
        1. Reference mineral candidates will have most of their peaks match peaks in the unknown both in position and intensity
        2. Reference mineral candidates may be eliminated if peaks greater than 30% relative intensity are missing from the unknown scan.
        3. Offsets in peak position may suggest a solid-solution series or a substitution in the crystal lattice. The software routines allow the search set up criteria to include these options. Repeat the search with new criteria that includes these options.
    iii. When a satisfactory match is determined, tag (or pin) that mineral to add it to the list of matches.
    iv. Continue down the list, searching for other minerals that have high percentage of matching peaks and account for unassigned peaks in the unknown scan. Typically after identifying all the readily resolved major and minor phases, an unknown can be identified by searching on

the unassigned peaks. Iterate until the majority of the peaks in the scan are assigned to a phase, typically all peaks with intensities above 20% of the most intense peak.

v. Identification of trace phases (<10%) may be difficult because typically only the primary or secondary peaks from the reference pattern may be resolved in the scan which means that identification is being made on limited spectral matching. In some cases, these identifications may need to be confirmed by concentrate samples or by another method.

5. Calibration and Quality Control Samples

None.

6. Limits, Precautions, and Interferences

Mineral identification by XRD is limited by the quality and quantity of reference phases included in the database. There will be differences between the actual mineral in the sample and the reference mineral, both in chemistry (substitutions) and crystallinity. This is particularly challenging in samples in which minerals are partially altered (weathering, diagenesis, laboratory treatment, etc.)

A typical detection limit for a mineral is approximately 3 weight percent (or it may be converted to volume percent by dividing the weight percent by the density of the mineral); however the limit varies among minerals depending upon several factors including: crystallinity, interference with other minerals, atomic substitutions, and other factors. Any real world sample will differ slightly from the reference mineral listed in the database. Thus there will be slight differences in peak position (two-theta) and intensity that result from any elemental substitutions, crystal defects, differences in sample preparation or data collection conditions. Some mineral XRD patterns are nearly identical, such as pyrite and sphalerite in which case additional data may be needed to confirm the identification.

In some cases, a peak may be observed in a pattern, but not assigned to a phase, indicating that at least one more phase is present in the material. Based on the position and character of the peak (intensity and shape), the phase may be limited to a small group of minerals. These are typically reported as a “questionable” phase and require further analysis and data to confirm their identity.

7. Acceptance of Data

In-house standards may be scanned and identified to confirm mineral species. Other data, including chemical, scanning electron microscopy, spectral or infrared spectroscopy may be necessary to confirm or support mineral identification.

8. Data Handling and Transfer

The XRD scan (in its original file format by the vendor) is stored in the Energy LIMS database. It can be viewed by PANalytical Data Viewer software which is available through the LIMS system.

Mineral identifications are listed in an Microsoft Excel™ spreadsheet sometimes with qualitative Major (>25%), minor (5-25%) and trace (<5%, confirmed) or "?" (possibly present but not confirmed) designations and entered into the Energy LIMS Database

9. References

FIZ/NIST Inorganic Crystal Structure Database, ICSD, NIST Standard Reference Database Number 84, National Institute of Standards and Technology, Gaithersburg, MD 20899, produced cooperatively with Fachinformationszentrum Karlsruhe, Germany

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10. Attachments

Appendix A – Step by Step Procedure for MDI Jade Software
Appendix B – Step by Step Procedure for Highscore Plus

11. History of Changes

R0: Initial Issue

Appendix A
Step by Step Procedure for MDI Jade Software

MDI Jade software has an extensive HELP manual with screen captures for all these steps. Please consult this HELP manual for detailed information on each window and the sub-routine options for data processing.

a. Launch the Jade software on the computer.

b. Under the File tab at top left of screen, select "Patterns". Upload a scan file from the directory in which it resides. The software can automatically read file formats from any of the XRD machines at the Denver Federal Center.

c. Model the background curve for the scan
   1. Under the "Analyze" tab at the top of the screen, select Fit Background routine. Adjust the background sampling frequency and fit-type (linear, exponential, or cubic spline) to yield a background simulation (shown in yellow) that approximates the true background of the pattern. If the algorithm does not model the background well, it may be manually adjusted by selecting the Background Edit icon and adding, deleting, relocating the red circles that define the background
   2. If necessary, select an appropriate value for the "BG Offset"
   3. Check the box "Strip K-alpha2"
   4. Select the "Remove Background" icon which will strip and subtract background from the displayed pattern.

d. Under the "Identify" tab at the top of the screen, select "Search/Match Setup" – this opens a window with numerous options which may be employed in the search match routine.

Appendix B
Step by Step Procedure for PANalytical HighScore Plus Software

PANalytical HighScore Plus software has an extensive HELP manual with screen captures for all these steps. Please consult this HELP manual for detailed information on each window and the sub-routine options for data processing.

a. Launch the HighScore Plus software on the computer.

b. Under the File tab at top left of screen, select “Open”. Upload a scan file from the directory in which it resides. The software can automatically read file formats from any of the XRD machines at the Denver Federal Center.

c. Model the background curve for the scan
   1. Under the “Treatment” tab at the top of the screen, select Strip K-alpha2 which opens a new box of options. Click the “Strip K-alpha2” icon to run the routine. Close the Strip K-alpha2 window
   2. Under the “Treatment” tab at the top of the screen, select Determine Background routine. Adjust the granularity and bending factor to yield a background simulation (shown in green) that approximates the true background of the pattern. If the algorithm does not model the background well, it may be manually adjusted by selecting the Manual tab and adding, deleting, and moving the black base point circles that define the background From the Manual tab, options are available to use Cubic Spline interpolation
   3. If necessary, select an appropriate value for the “BG Offset” located under the “More” icon.
   4. Select the “Subtract” icon which will subtract background from the displayed pattern.

d. This step is not necessary to perform a Search & Match routine; however it may helpful to the analyst during manual searches. Under the “Treatment” tab at the top of the screen, select the Search Peaks icon. From the Search Peaks window, adjust the criteria for a peak search (minimum significance, minimum tip width, maximum tip width, peak base width and the method) and perform a Peak Search by clicking the icon. These steps may be repeated adjusting the search criteria until a majority of the peaks are accounted in the peak list shown on the display by the dashed lines.

e. Under the “Analysis” tab at the top of the screen, select the Search & Match routine. From the Search & Match window, set criteria (restrictions, Scoring scheme, Two theta shift, and Automatic Identify settings) and execute a search by clicking the Search icon. Close the Search & Match window.

f. The Search & Match routine will return a list of possible mineral matches sorted by score for best fit according the search criteria. Highlight each mineral in the list starting at the top and evaluate whether the reference pattern is a candidate. Selected candidates from the list can be moved to the Accepted Pattern list by dragging the highlighted pattern with a left mouse click up. The "Additional Graphics" window displays the Residue pattern after subtraction of the accepted patterns from the original scan. Continue reviewing, selecting, and if necessary completing new Search & Match routine with modified criteria until almost all the peaks in the original scan are accounted.